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Application of Z-dependent perturbation theory to autoionizing states of heliumlike atoms: Feshbach projection method

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The $2s2p\ ^1P$ and ^3P autoionizing states of heliumlike ions are studied via an implementation of the Feshbach projection method within the framework of Z-dependent perturbation theory. These same states are also studied by a more straightforward (nonprojected) application of Z-dependent perturbation theory that has features similar to those of the stabilization method. The computational and theoretical advantages of applying the Feshbach method within Z-dependent perturbation theory are emphasized. Results for all two-electron ions with $Z=2$ to 10 are tabulated and compared with experiment and with other very accurate theoretical results for these systems. Included in these results are estimates of the resonance positions, energy "shifts," and widths of these autoionizing states.

I. INTRODUCTION

Autoionizing states of atoms present special theoretical and computational problems. Of the methods that have been applied to the study of such atomic states, one of the most popular and effective has been the Feshbach projection method.[1] Much recent work in this area is summarized in the review articles of Temkin and Bhatia.[2] In the present paper we study autoionizing states via Z-dependent perturbation theory and the variational perturbation method. Perturbation theory is perhaps computationally more naturally suited to the study of autoionizing states than approaches based on the variational method. Indeed, the description of these states by Fano[3] was based on a perturbation picture of the interaction between an isolated discrete state and an adjacent continuum. The method proposed by Feshbach and applied to atomic systems by Hahn, O'Malley, and Spruch[4] and O'Malley and Geltman[5] has a ready and obvious implementation in perturbation theory. Indeed, the method is even more precisely realized in perturbation theory than in its usual variational manifestation. In particular, it should be emphasized that the Feshbach projection operators for multielectron systems, which for systems with more than two electrons are difficult to construct within the variational approach, are as easy to construct in the variational perturbation method for an atom with an arbitrary number of electrons as for one with two electrons. The present paper presents an application of the variational perturbation implementation of this approach to the $2s2p$ singlet and triplet autoionizing states of heliumlike ions. The resonance positions and widths for these states are calculated and compared with experimental values where available, and with the very accurate results of Bhatia and Temkin[6,7] and Chung and Davis[8] for the neutral atom, and the comparably accurate results of Ho[9] for the ions through Ne^{8+}. In addition, a "nonprojected" version of this calculation is performed in order to compare and contrast this more direct method, analogous to the stabilization method, to the Feshbach method for these states. Comparison of these two results yields estimates of the energy "shifts" for these autoionizing states.

II. METHOD

A. Z-dependent perturbation theory

In Z-dependent perturbation theory, the nonrelativistic Hamiltonian for an N electron atom is given, in charge-scaled atomic units, by

$$H=H_0+\frac{1}{Z}H_1\ , \tag{1}$$

where the zeroth-order Hamiltonian is

$$H_0=\sum_{i=1}^{2}\left[-\tfrac{1}{2}\nabla_i^2-\frac{1}{r_i}\right]\ , \tag{2}$$

and the perturbation is

$$H_1=\frac{1}{r_{12}}\ . \tag{3}$$

The nonerelativistic energy and wave function are then given by

$$E=\sum_{n=0}^{\infty}Z^{-n}\varepsilon_n\ , \tag{4a}$$

$$\Psi=\sum_{n=0}^{\infty}Z^{-n}\psi_n\ . \tag{4b}$$

The variational perturbation method consists of optimizing the nth-order variational wave function $\tilde{\psi}_n$ via a functional[10] which yields an upper bound to ε_{2n} and an estimate of ε_{2n+1}:

$$\varepsilon_{2n} \le \langle \tilde{\psi}_n | G_0 | \tilde{\psi}_n \rangle + 2 \langle \tilde{\psi}_n | G_1 | \psi_{n-1} \rangle - \sum_{k=2}^{2n-1} \varepsilon_k \sum_{i=n-k}^{n} \langle \psi_{2n-k-i} | \psi_i \rangle , \tag{5}$$

$$\varepsilon_{2n+1} \approx \langle \tilde{\psi}_n | G_1 | \tilde{\psi}_n \rangle - \sum_{k=2}^{2n} \varepsilon_k \sum_{i=n+1-k}^{n} \langle \psi_{2n+1-k-i} | \psi_i \rangle . \tag{6}$$

In the above, $G_i = H_i - \varepsilon_i$ and terms with negative indices are to be ignored. If Eq. (5) is to yield an upper bound to ε_{2n} for an excited state, the approximate nth-order wave functions have to satisfy the perturbational equivalent[11] of the orthogonality conditions imposed on variational trial wave functions:

$$\langle \tilde{\psi}_n^{(N)} | \psi_0^{(\alpha)} \rangle = \langle \psi_n^{(N)} | \psi_0^{(\alpha)} \rangle = - \frac{\langle \psi_0^{(N)} | H_1 | \psi_0^{(\alpha)} \rangle}{\varepsilon_0^{(N)} - \varepsilon_0^{(\alpha)}} , \quad \alpha = 1, \ldots , N-1 . \tag{7}$$

The superscripts in Eq. (7) are state labels with N denoting the state of interest, states denoted by α being lower-lying states. For ordinary excited states, this condition is easily satisfied by including the exact zeroth-order wave functions of all the lower-lying states in the basis set of the trial wave function. Autoionizing states like the $2s2p$ states of helium, however, possess an infinite number of lower-lying discrete and continuum states and such a procedure is clearly impossible.

B. Feshbach projection method

The Feshbach projection method defines a pair of orthogonal projection operators, Q and P, such that

$$\lim_{r_1, r_2 \to \infty} Q\psi \to 0 , \tag{8a}$$

$$\lim_{r_1, r_2 \to \infty} P\psi \to \psi , \tag{8b}$$

$$Q + P = 1 . \tag{8c}$$

For a two-electron atom, O'Malley and Geltman[5] took the projection operators to be $P = P_1 + P_2 - P_1 P_2$, $Q = 1 - P$ with $P_i = | 1s(i) \rangle \langle 1s(i) |$ for an autoionizing state lying between the $n=1$ and 2 ionization thresholds. The initial computational task in implementing the method is then[2] to obtain the eigenfunctions and eigenvalues of $H_{QQ} = QHQ$. The eigenfunctions are utilized to form $Q = \sum | \Psi_Q \rangle \langle \Psi_Q |$ which in turn permits calculation of the "shift" Δ and the width Γ for the state of interest, while the eigenvalue e_Q yields an estimate of the resonance position $E = e_Q + \Delta$. The accuracy of e_Q as an estimate of the resonance position then depends on the magnitude of the shift, Δ. Since the eigenfunctions of H_{QQ} are square-integrable functions, the calculation proceeds in the manner of a standard variational calculation for a bound state with one additional complication: the need to project out any $1s$ character from the basis set. The optimization of any parameters in the basis set is stable against "variational collapse" to lower-lying, singly excited states of the system since projection has made the trial wave function very nearly orthogonal to all lower-lying states, bound or continuum, at least in that region of configuration space where there is significant overlap between $Q\psi$ and the wave functions of these singly excited states. Nevertheless, it should be noted that in this standard variational approach to the Feshbach method, the possibility does exist for "collapse" to an e_Q corresponding to the $Q\psi$ part of a singly excited state, since these states are only approximately described as $1s$ in character ($1s$ a hydrogenic orbital).[12] It should also be said that in practice this does not appear to be a significant hindrance to the accuracy of the method.

Application of the Feshbach projection method within the variational perturbation method is quite straightforward. In this instance the trial nth-order wave function for $Q\psi$ must yield an upper bound to the ε_{2n} since the condition that the $\tilde{\psi}_n$ must satisfy, Eq. (7), involves only the exactly known, zeroth-order wave functions for all lower-lying states. These zeroth-order functions are precisely $1s$ in character so that the $Q\tilde{\psi}_n$ are all independent of these conditions. Hence application of the variational perturbation method to the $Q\tilde{\psi}_n$ within the Feshbach projection method yields rigorous upper bounds to the even-order expansion coefficients of doubly excited states without the possibility of variational collapse to lower-lying, singly excited states. The method is thus inherently more accurate than application of the straightforward variational method.[13] It should be clear that although the optimization of the variational wave functions is accomplished via a method yielding an upper bound for the energy coefficients of even order, the approximate energy eigenvalue obtained by summing the perturbation series of Eq. (4a) is not necessarily an upper bound to the corresponding eigenvalue of H_{QQ}.

As the variational perturbation method is particularly suited to the study of excited states in general, it can be expected that it should also be advantageous for the study of doubly excited states. Indeed, the present implementation of the Feshbach method can be easily extended to the calculation of more highly excited autoionizing states. Finally, of course, the $1/Z$ expansion has the great advantage of yielding values for an entire isoelectronic sequence from a single calculation.

If one now considers how these results might generalize for more complex atoms, the advantages of the variational perturbation method become even more apparent. The projection operators required by the variational perturbation method for systems containing more than two electrons still need only be constructed from hydrogenic orbitals, whereas constructing the projection operators for an N-electron autoionizing state in the variational method will require the $(N-1)$-electron wave function of the target. For example, a doubly excited state of a lithiumlike ion requires only terms involving $1s(i)1s(j)$, $i,j = 1,2,3$ in the projection operators in place of terms involving $\Psi^{(1\,{}^1S)}(i,j)$, which can only be known approximately. Furthermore, the results obtained for a two-electron atom by this method are directly transferable to any complex atom containing the same two-electron configuration as a subconfiguration.[14]

III. RESULTS AND DISCUSSION

With the exception of Table VII, where the data are given in Å, all tabulated results in this paper are expressed in atoms units. Two sets of calculations are presented here for the $2s2p$ autoionizing states of two-electron ions. The first, based on the projection formalism of the preceding section, has all the characteristics of a conventional variational perturbation calculation for an ordinary bound state. The second, a straightforward (no projection) calculation, is the variational perturbation version of the stabilization method and exhibits behavior analogous to the "avoided crossings" associated with variational collapse in that method. Both of the present calculations utilize variational wave functions of the form

$$\tilde{\psi}_n = A + r_{12}B \ , \tag{9a}$$

with A and B both of the form

$$\sum_{n+m+l=0}^{N} c_{nml}(1 \pm P_{12}) r_1^{n+l} r_2^{m+l+1} P_l(\cos\theta_{12}) \times \exp[-\alpha_n(r_1+r_2)]\cos\theta_2 \ . \tag{9b}$$

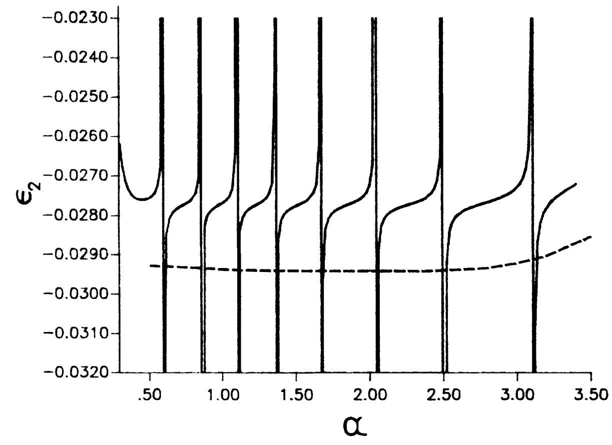

FIG. 1. The ε_2 optimization curves for the $2s2p$ ^3P autoionizing state: solid line, nonprojected ε_2; dashed line, projected ε_2.

For the projected wave functions, however, variational convergence was found to be excellent without including terms like $r_{12}B$ in the trial wave function. This considerably simplifies the construction of $Q\tilde{\psi}_n$. The final basis sets utilized include terms with $n+m+l \leq 12$ and 14 for a total of 504 "A and B-type" and 372 "A-type" terms for the "nonprojected" and projected wave functions, respectively. The procedure followed here was to first obtain the "optimum" α_1 for the trial first-order wave function that yielded the minimum ε_2. Optimization curves for these two calculations are displayed in Fig. 1. Optimization of $Q\tilde{\psi}_1$ is straightforward, but optimization of the nonprojected wave function is complicated considerably by the appearance of singular points similar to the avoided crossings that are characteristic of the stabilization method. In this latter case the procedure followed was to choose an α_1 between $\frac{1}{2}$ and 3 which corresponded to the minimum slope in the optimization curve, rather than the minimum value of ε_2. This corresponds to somewhat arbitrarily choosing one of several inflection points in the ε_2 versus α_1 curve. Setting $\alpha_n = \alpha_1$, the higher-order $\tilde{\psi}_n$ and ε_n are then easily generated recursively, since a single diagonalization of the G_0 matrix is sufficient to obtain the linear parameters for all the $\tilde{\psi}_n$.[15] Energy expansion coefficients for these two methods are exhibited in Table I. Although the two sets of coefficients are not directly comparable, coefficients generated by each method for the two states considered here display similar behavior. The convergence of the triplet state energy coefficients in particular is remarkably rapid. The slowly damped oscillation of the higher-order coefficients for the singlet state is more typical of the behavior found for most singly excited states.[11(b),16] The only other such calculation of higher-order coefficients for doubly excited states is due to Drake and Dalgarno.[17] Since the latter calculation, based as it is on the method of Miller,[18] utilizes an entirely different projection operator, we might not expect much similarity between the projected energy coefficients obtained here and those of Ref. 17. In fact, it appears that the latter coefficients are more closely related to the nonprojected coefficients found here, at least for the low-order coefficients.

We can also extract a few of these perturbation energy coefficients from the complex-rotation calculations of Ho.[9] Those calculations extend over a sufficient range of Z so that differencing of the energy eigenvalues yields reliable estimates of the expansion coefficients implicit in the data. These are also included in Table I where they should be compared to the present nonprojected results. In obtaining these coefficients, the contributions to the energy of the exact zeroth- and first-order coefficients were first removed from the data, so that the leading coefficient was ε_2. The agreement between the present nonprojected energy coefficients and those extracted from Ho's data is entirely satisfactory given the uncertainties in obtaining an "optimum" ε_2 with the present method on the one hand, and the relatively large rms deviations for the estimates of the energy coefficients obtained from Ho's data on the other.

The accuracy of the ε_2 obtained here is estimated by observing the variational convergence of ε_2 as the size of the basis set utilized for the trial, first-order wave function is increased. On this basis, the values of ε_2 presented in Table I are listed to one more significant figure than can be considered reliable. As the higher-order coefficients cannot be more accurate than ε_2, all subsequent energy coefficients are arbitrarily truncated to the same number of decimal places as ε_2, although the highest-order coefficients listed are unlikely to be this accurate.

The ε_2 calculated here can also be compared to a num-

TABLE I. The ε_n for the $2s2p$ singlet and triplet states.

	$2s2p\ ^1P$				$2s2p\ ^3P$			
n	Projected[a]	Nonprojected[a]	DD[b]	Ho[c]	Projected[a]	Nonprojected[a]	DD[b]	Ho[c]
0	−0.250 000 00	−0.250 000 00			−0.250 000 0	−0.250 000 0		
1	0.191 406 25	0.191 406 25			0.132 812 5	0.132 812 5		
2	−0.095 85	−0.096 76	−0.097 637	−0.096 688	−0.029 431 2	−0.027 739 5	−0.027 792 4	−0.027 726 4
3	0.049 22	0.050 39	0.051 671	0.050 322	0.005 119 6	0.003 635 2	0.003 529 0	0.003 652 1
4	−0.012 95	−0.007 88	−0.013 509	−0.016 398	−0.000 805 4	−0.000 532 5	−0.000 624 9	−0.000 986 3
5	−0.014 67	−0.030 72	−0.018 191		−0.000 244 3	−0.000 135 1	−0.000 080 0	
6	0.017 49	0.040 57	0.022 122		0.000 110 6	−0.000 000 9	0.000 001 2	
7	0.000 34	−0.027 25	−0.005 574		0.000 002 6	−0.000 016 0	−0.000 028 2	
8	−0.014 97	0.032 50	−0.011 257		−0.000 005 9	0.000 015 2	−0.000 011 0	
9	0.010 21	−0.087 27	0.007 149		0.000 009 6	−0.000 024 7	−0.000 007 3	
10	0.008 04		0.012 453		0.000 002 5		−0.000 004 0	
11	−0.016 76		−0.023 726		−0.000 000 6		−0.000 002 1	
12	0.003 23		0.001 002		0.000 000 04		−0.000 001 1	
13	0.016 72				−0.000 000 1			
14	−0.016 41				−0.000 000 2			
15	−0.007 57				−0.000 000 07			

[a] This calculation.

[b] Drake and Dalgarno, Ref. 17.

[c] Obtained from the results of Ho, Ref. 9.

TABLE II. Comparison of some second-order results for the $2s2p$ states.

Quantity	$2s2p$ ^1P Present paper	$2s2p$ ^1P Other	$2s2p$ ^3P Present paper	$2s2p$ ^3P Other
Projected energy ε_2	−0.095 85	−0.0955[a] −0.095 598[b]	−0.029 431 2	−0.029 44[a] −0.029 420 4[b]
Nonprojected energy ε_2	−0.096 76	−0.0960[a] −0.096 871[c]	−0.027 739 5	−0.028 60[a] −0.027 688[c]
Shift Δ_2	−0.000 91	−0.000 407 731 1[d]	0.001 691 7	0.001 697 175[d]
Width Γ_2	0.004 901 05	0.004 796[e] 0.004 627[f]	0.000 329 781	0.000 325 4[e]

[a] Chan and Stewart, Ref. 19.
[b] Knight, Ref. 21.
[c] Vainshtein and Safronova, Ref. 20.
[d] Exact result of Horak and Lewis, Ref. 22.
[e] Obtained from the results of Ho, Ref. 9.
[f] Macias and Riera, Ref. 24.

ber of ε_2 obtained by other workers by a variety of methods. This is done in Table II for both projected and nonprojected ε_2. The results of Chan and Stewart[19] are variational perturbation calculations with a hydrogenic basis set and include both projected and nonprojected values, while the calculations of Vainshtein and Safronova[20] are based on diagrammatic perturbation theory. The results of Knight[21] for the projected ε_2 are corrected here for the explicit inclusion of a $1s2p$ term in his configuration-interaction (CI) basis. The variational convergence of the present ε_2, together with the accuracy of the total energies obtained with them, suggest that these ε_2 are more accurate than the other ε_2 presented in Table II, both for the projected and nonprojected calculations.

Energy Shifts. The difference between the projected ε_n and the nonprojected ε_n of Table I is just the nth-order contribution to the shift, Δ_n, of the Feshbach method. The Δ_2 for the two states considered here have been calculated essentially exactly by Horak and Lewis[22] and by Sharma and co-workers.[13,23] Their exact results are compared to the present results in Table II. The present results for the triplet state are quite satisfactory, while the results for the singlet state suggest larger errors in the ε_2 for this state. This is more likely to be due to inaccuracies in the nonprojected singlet ε_2, given the difficulty in optimizing ε_2 with this method. However, comparison with the ε_2 extracted from the data of Ho indicates that the nonprojected ε_2 is not so inaccurate as to produce the error observed in Δ_2. This is confirmed by the accuracy obtained for the total energies with this ε_2, especially for the higher-Z members of the isoelectronic sequence where errors due to higher-order coefficients are suppressed. Nevertheless, it is difficult to ascribe an error of 5 units in the fourth decimal to the projected ε_2 alone. More than likely, this error in Δ_2 must be shared by both of the ε_2 for this state. The higher-order expansion coefficients of the shift can be obtained by taking the difference of the projected and nonprojected energy coefficients of Table I. These appear to be small in magnitude and hence are probably not particularly accurate given the limited accuracy of the ε_n. Nevertheless, one can obtain an estimate of the total shift for members of the isoelectronic sequence with $Z > 10$ from this data, and they are presented in Table III.

TABLE III. The Δ_n for the $2s2p$ singlet and triplet states.

n	$2s2p$ ^1P	$2s2p$ ^3P
2	−0.000 91	0.001 691 7
3	0.001 17	−0.001 484 4
4	0.005 07	0.000 272 9
5	−0.016 05	0.000 109 2
6		−0.000 111 5
7		−0.000 018 6
8		0.000 021 1
9		−0.000 034 3

Widths. For the $1/Z$ expansion, the lowest-order contribution to the width is found to be of second order (in charge-scaled atomic units):

$$\Gamma_2 = 2\pi \left| \left\langle \psi_0^{2s2p} \left| \frac{1}{r_{12}} \right| \psi_0^{1skp} \right\rangle \right|^2 , \tag{10}$$

where ψ_0^{1skp} is a hydrogenic continuum function degenerate in energy with the ψ_0^{2s2p} state. This Γ_2 can be calculated exactly and details of this calculation are presented in the Appendix, while the results are included in Table II. Higher-order coefficients for the width are calculated here by expanding the expression for the total width,

$$\Gamma = 2\pi \left| \left\langle Q\psi \left| \frac{1}{r_{12}} \right| P\psi \right\rangle \right|^2 . \tag{11}$$

We approximate $P\psi$ (here expressed in atomic units) by

$$P\psi \approx 2^{-1/2}(1 \pm P_{12})\psi_{1s(Z)}\psi_{kp(Z-1)} . \tag{12}$$

The continuum function $\psi_{kp(Z-1)}$ has the correct asymptotic behavior to represent $P\psi$. In charge-scaled atomic units it can be written as $\psi_{kp(1-1/Z)}$. In these units, $\frac{1}{2}k^2 = E(Z) + \frac{1}{2}$, the difference in energy between the res-

TABLE IV. The Γ_n for the $2s2p$ singlet and triplet states.

			$2s2p\ ^1P$		
n	$\sigma=1.00$[a]	$\sigma=0.88$[a]	Ho[b]	DD[c]	MR[d]
2	0.004 901 08	0.004 901 07	0.004 79	0.004 89	0.004 63
3	−0.011 06	−0.010 81	−0.009 50	−0.010 46	−0.008 86
4	0.009 13	0.008 58	0.005 63	0.006 78	0.004 99
5	−0.001 74	−0.001 01			
6	−0.002 58	−0.003 31			
7	0.001 27	0.001 65			
8	0.001 02	0.001 01			

		$2s2p\ ^3P$		
n	$\sigma=1.00$[a]	$\sigma=0.72$[a]	Ho[b]	DD[c]
2	0.000 329 781	0.000 329 776	0.000 327	0.000 327
3	0.000 576	0.000 044	−0.000 014	0.000 152
4	−0.000 133	−0.000 209	−0.000 091	−0.000 124
5	−0.000 508	−0.000 023		
6	−0.000 007	0.000 049		
7	0.000 164			
8	0.000 061			
9	−0.000 057			

[a] Present paper.

[b] Obtained from the results of Ho, Ref. 9.

[c] Drake and Dalgarno, Ref. 17.

[d] Macias and Riera, Ref. 24.

TABLE V. Resonance positions for the $2s2p\ ^1P$ states.

	Projected		Nonprojected			
Z	PP[a]	Other	PP[a]	Ho[b]	Other	Experiment
2	−0.692 54	−0.692 894 7[c] −0.692 773[e]	−0.693 05	−0.693 136	−0.639 157[c] −0.693 024[e] −0.693 54[g] −0.692 8[h] −0.692 13[i]	−0.693 71±0.000 55[d] −0.692 94±0.000 37[f]
3	−1.757 01	−1.757 243[j]	−1.757 36	−1.757 558	−1.757 51[j] −1.758 13[g] −1.754 00[i]	−1.7565±0.002[k] −1.756±0.001[l]
4	−3.318 89		−3.319 37	−3.319 480	−3.320 15[g] −3.314 11[i]	
5	−5.379 58		−5.380 15	−5.380 21	−5.380 93[g] −5.373 54[i]	
6	−7.939 62		−7.940 26	−7.940 28	−7.941 03[g] −7.932 30[i]	
7	−10.999 27		−10.999 95	−10.999 96	−11.000 73[g] −10.991 6[i]	
8	−14.558 67		−14.559 39	−14.559 39	−14.560 17[g] −14.550 4[i]	
9	−18.617 87		−18.618 64	−18.618 67	−18.619 43[g]	
10	−23.176 97		−23.177 76	−23.177 77	−23.178 56[g]	

[a] Present paper.

[b] Ho, Ref. 9.

[c] Bhatia and Temkin, Ref. 6.

[d] Madden and Codling, Ref. 26.

[e] Chung and Davis, Ref. 8(b).

[f] Morgan and Ederer, Ref. 27.

[g] Drake and Dalgarno, Ref. 17.

[h] Oza, Ref. 25.

[i] Macias and Riera, Ref. 24.

[j] Bhatia, Ref. 7.

[k] Carroll and Kennedy, Ref. 28.

[l] Zeim, Bruch, and Stolterfoht, Ref. 29.

onance position of the $2s2p$ state and the $1s$ hydrogenic orbital. Expanding $Q\psi$, $P\psi$, and k^2 as power series in $1/Z$ yields, in charge-scaled units,

$$\Gamma=\sum_{n=2} Z^{-n}\Gamma_n \, , \tag{13}$$

with Γ_2 given by Eq. (10) with k^2 taking on its zeroth-order value of $\frac{1}{2}$. Since the total width is to be multiplied by Z^2 in converting back to conventional atomic units, Γ_2 represents the limiting value of Γ for high-Z ions. These Γ_n are presented in Table IV. Widths for these ions are available from the calculations of Ho.[9] Differencing Ho's values for $Z=2$ to 10, one can obtain the lowest-order coefficients of the Z expansion of Γ. The values for Γ_2 so obtained are also presented in Table II, while higher-order coefficients are presented in Table IV. Also included in this table are values for the Γ_n obtained from the results of Drake and Dalgarno.[17] Macias and Riera[24] have utilized a "discretization" method to study autoionizing states of atoms. Their results are to be compared to the present nonprojected results. They extract the $1/Z$ expansion coefficients for the energy and width from their results for $Z=2$ to 8 for the $2s2p\ {}^1P$ state. Their ε_2 of -0.0772 is in error in the first significant figure, but their Γ_2 of 0.00462 is in much better agreement with the present exact Γ_2. This is probably due to their not having utilized the exact values of ε_0 and ε_1 in obtaining their estimate of ε_2, while Γ_2 is the leading term of the $1/Z$ expansion for the width.

Resonance positions. The total energies obtained by the two methods of this paper for the $2s2p\ {}^1P$ and ${}^3P$ autoionizing states are presented in Tables V and VI. These are compared to theoretical values of the resonance position obtained by other workers as well as some low-Z values obtained primarily from electron spectroscopy or photoionization experiments. The theoretical values of Ho[9] and Macias and Riera[24] as well as the experimental values are to be compared to the nonprojected results obtained in the present calculation, while the values obtained by Bhatia and Temkin[6,7] with the Feshbach projection method and the results of the saddle-point method of Chung and Davis[8] are to be compared to the projected results. The saddle-point method of Chung and Davis does not precisely correspond to the Feshbach method as implemented by O'Malley and Geltman, but the difference apparently is rather small. In particular, it is easy to develop the $1/Z$ expansion for the wave function in the saddle-point method. One finds that the first-order correction to the wave function differs from that of the present method by the inclusion of a single extra term proportional to a hydrogenic $1s2p$ function. The energy values tabulated in Tables V and VI indicate that the results obtained here with the nonprojected wave function are surprisingly good, despite the difficulties inherent in optimizing that wave function. The agreement with the data of Ho is particularly striking. Agreement with the singlet P results of Macias and Riera is consistent with errors in their values of ε_0, ε_1, and ε_2. As these were obtained from their data by differencing they are implicit in their energy values. Also included for comparison are the energy eigenvalues obtained by Drake and Dalgarno[17] which appear to be more accurate than the results of Macias and Riera but not as accurate as those of Ho. Their

TABLE VI. Resonance positions for the $2s2p\ {}^3P$ states.

	Projected		Nonprojected			
Z	PP[a]	Other	PP[a]	Ho[b]	Other	Experiment
2	−0.761 471	−0.761 491[c]	−0.760 44	−0.760 492	−0.760 492[c]	−0.7605±0.0011[d]
		−0.761 457[e]			−0.760 570[f]	−0.7609±0.0011[g]
					−0.760 451 1[h]	
3	−1.879 384	−1.879 395[i]	−1.878 15	−1.878 179	−1.878 15[i]	−1.877±0.001[j]
					−1.878 251[f]	−1.881±0.02[k]
4	−3.496 955		−3.495 61	−3.495 632 7	−3.495 700[f]	
5	−5.614 376		−5.612 97	−5.612 99	−5.613 050[f]	
6	−8.231 723		−8.230 27	−8.230 28	−8.230 347[f]	
7	−11.349 027		−11.347 54	−11.347 55	−11.347 614[f]	
8	−14.966 302		−14.964 79	−14.964 80	−14.964 861[f]	
9	−19.083 526		−19.082 03	−19.082 04	−19.082 096[f]	
10	−23.700 775		−23.699 25	−23.699 26	−23.699 321[f]	

[a] Present paper.
[b] Ho, Ref. 9.
[c] Bhatia and Temkin, Ref. 6.
[d] Hicks and Comer, Ref. 30.
[e] Chung and Davis, Ref. 8(a).
[f] Drake and Dalgarno, Ref. 17.
[g] Gelebart, Tweed, and Peresse, Ref. 31.
[h] Oza, Ref. 25.
[i] Bhatia, Ref. 7.
[j] Zeim, Bruch, and Stolterfoht, Ref. 29.
[k] Bruch *et al.*, Ref. 32.

TABLE VII. Comparison with observed wavelengths (in Å) for the $2s2p$-$1s2s$ transitions.

	$2s2p\ ^1P$–$1s2s\ ^1S$		$2s2p\ ^3P$–$1s2s\ ^3S$	
Z	PP[a]	Experiment	PP[a]	Experiment
4	77.6657		78.5216	78.512±0.01[b] 78.530[c]
5	49.5175		49.9378	49.935±0.004[b]
6	34.2878	34.286±0.006[b] 34.29[d]	34.5249	34.523±0.004[b] 34.52[d] 34.525[e]
7	25.1337	25.125±0.006[b]	25.2806	25.276±0.003[b]
8	19.2073	19.207±0.003[b]	19.3046	19.301±0.006[b]
9	15.1525	15.155[f]	15.2202	15.217[d] 15.224[f]
10	12.2570		12.3060	12.303[g]
11	10.1176	10.119[h]	10.1542	10.157[h]
12	8.4923	8.4910[i] 8.493[h]	8.5204	8.518[j] 8.5228[i] 8.521[h]
13	7.2287	7.2282[i] 7.231[h]	7.2507	7.2518[i] 7.251[h]
14	6.2269	6.213[j] 6.230[h]	6.2445	6.236[j]
15	5.4193		5.4336	
16	4.7588		4.7706	
17	4.2118		4.2215	
18	3.7535		3.7617	
19	3.3659		3.3729	
20	3.3051		3.0411	
21	2.7506		2.7557	
22	2.5040	2.5044[k]	2.5085	2.509[l]

[a] Present paper.
[b] Nicolosi and Tondello, Ref. 33.
[c] Goldsmith, Ref. 39.
[d] Peacock, Hobby, and Galanti, Ref. 34.
[e] Feldman and Cohen, Ref. 40.
[f] Feldman *et al.*, Ref. 35.
[g] Peacock, Speer, and Hobby, Ref. 41.
[h] Feldman *et al.*, Ref. 36.
[i] Aglitsky *et al.*, Ref. 37.
[j] Walker, Rugge, and Weiss, Ref. 38.
[k] Bitter *et al.*, Ref. 42.
[l] Turechek and Kunze, Ref. 43.

TABLE VIII. Widths for the $2s2p\ ^1P$ states.

Z	$\sigma=1.00$[a]	$\sigma=0.88$[a]	Ho[b]	DD[c]	Other	Experiment
2	0.001 33	0.001 37	0.001 36	0.001 34	0.001 33[d] 0.001 373[f] 0.001 33[h] 0.001 37[j]	0.0014±0.0001[e] 0.0015±0.0007[g] 0.0015±0.0003[i] 0.0014±0.0007[k]
3	0.002 14	0.002 18	0.002 19	0.002 17	0.002 18[l] 0.002 20[j]	0.0028±0.0009[m]
4	0.002 67	0.002 71	0.002 73	0.002 71	0.002 71[j]	
5	0.003 04	0.003 07	0.003 09	0.003 07	0.003 05[j]	
6	0.003 30	0.003 33	0.003 35	0.003 34	0.003 28[j]	
7	0.003 50	0.003 53	0.003 53	0.003 53	0.003 46[j]	
8	0.003 66	0.003 68	0.003 69	0.003 69	0.003 59[j]	
9	0.003 78	0.003 80	0.003 81	0.003 81		
10	0.003 88	0.003 90	0.003 90	0.003 91		

[a] Present paper.
[b] Ho, Ref. 9.
[c] Drake and Dalgarno, Ref. 17.
[d] Bhatia and Temkin, Ref. 6.
[e] Madden and Codling, Ref. 26.
[f] Chung and Davis, Ref. 8(b).
[g] Hicks and Comer, Ref. 30.
[h] Oza, Ref. 25.
[i] Gelebart, Tweed, and Peresse, Ref. 31.
[j] Macias and Riera, Ref. 24.
[k] Morgan and Ederer, Ref. 27.
[l] Bhatia, Ref. 7.
[m] Carroll and Kennedy, Ref. 28.

results appear to be consistently too negative for both the singlet and triplet states. This is consistent with their ε_2 also appearing to be too negative. The resonance positions are also compared with experimental values where these are available. These are consistent with the theoretical results which are generally of higher accuracy.

For high-Z values, experimental wavelengths for radiative transitions to the singlet or triplet $1s2s$ state are available. Comparisons to the present results are presented in Table VII. The theoretical wavelengths are calculated using energies for the $1s2s$ states taken from the work of Sanders and Knight[16] and including lowest-order, one-electron relativistic corrections for both states. These calculated wavelengths are in excellent agreement with the observed wavelengths, with the agreement improving as Z increases and the contribution of the less-accurate higher-order energy coefficients becomes less important.

Total widths. Finally, Tables VIII and IX present the total widths obtained here with Eq. (11) for the states under consideration. These are also compared with other theoretical and experimental results. The values obtained here for the widths of the $2s2p$ singlet state are quite good. The results for the triplet state are less satisfactory, perhaps due to the approximate nature of the $P\psi$ utilized here. Since the widths for the triplet state are an order of magnitude smaller than those for the singlet, they are more likely to be sensitive to errors in the higher-order coefficients. However, Drake and Dalgarno[17] utilized the same $P\psi$ with a screening parameter of 1 in their perturbation calculation achieving better results for the triplet state.

In the present case, we have introduced a variable screening parameter for the continuum function alone, so that it becomes, in atomic units, $kp(Z-\sigma)$. Although this function no longer has the correct asymptotic behavior for $P\psi$, it might better represent $P\psi$ in that region of coordinate space where the integrand of the matrix element for the width is largest. Although there is no clear-cut way to select the optimum σ for this purpose, the values of σ utilized in the tables were selected with an eye toward obtaining accurate values of the width for low Z, where the higher-order Γ_n contribute most significantly to the width. In doing this, a greater weight was assigned to the widths obtained by Bhatia and Temkin[6,7] with the Feshbach method. Although it is possible to choose σ so as to reproduce a particular value of Γ for a single value of Z, such a choice of σ does not generally give good values of Γ over the range of values of Z presented in the tables. The σ utilized here were chosen so as to also give reasonable values of the width for the larger Z. It is interesting to note that this procedure yielded excellent agreement with the very accurate results of Chung and Davis[8] for the singlet state of helium. It should be kept in mind that, for increasing values of Z, these perturbation results will necessarily yield increasingly accurate (nonrelativistic) values of the width.

IV. SUMMARY

The implementation of the Feshbach projection method presented here has all the advantages of efficiency and computational ease ascribed to Z-dependent perturbation theory. It provides in a single calculation the results for an entire isoelectronic sequence. In addition, results obtained for an n-electron system can be directly incorporated (with the appropriate coupling coefficients) into all complex systems which contain the same n-electron configuration as a subsystem. The variational perturbation approach is particularly suited to the study of excited states and the doubly excited states of the type considered here are no exception. The present method is easily extended to more highly excited autoionizing states. Computationally, the variational perturbation method has advantages over the variational method as there is no secular determinant to solve; only a simple

TABLE IX. Widths for the $2s2p\ ^3P$ states.

Z	$\sigma=1.00$[a]	$\sigma=0.72$[a]	Ho[b]	DD[c]	Other	Experiment
2	0.000 524	0.000 300	0.000 297	0.000 374	0.000 327[d] 0.000 301[f]	< 0.000 55[e] 0.000 37[g]
3	0.000 488	0.000 321	0.000 312	0.000 364	0.000 328[h]	
4	0.000 457	0.000 328	0.000 318	0.000 357		
5	0.000 435	0.000 330	0.000 320 7	0.000 352		
6	0.000 420	0.000 331	0.000 322	0.000 349		
7	0.000 408	0.000 332	0.000 323	0.000 346		
8	0.000 399	0.000 332	0.000 323	0.000 344		
9	0.000 391	0.000 332	0.000 324	0.000 343		
10	0.000 385	0.000 332	0.000 324 2	0.000 341		

[a] Present paper.
[b] Ho, Ref. 9.
[c] Drake and Dalgarno, Ref. 17.
[d] Bhatia and Temkin, Ref. 6.
[e] Hicks and Comer, Ref. 30.
[f] Oza, Ref. 25.
[g] Gelebart, Tweed, and Peresse, Ref. 31.
[h] Bhatia, Ref. 7.

system of linear equations. Hence, if in the study of doubly excited states no projection operator is utilized, one has the analog of the stabilization method but without the confusion of multiple roots. If, instead, a projection operator of the type introduced by O'Malley and coworkers[4,5] is utilized, the optimization of the perturbation wave functions yields rigorous upper bounds to the even-order energy coefficients of these autoionizing states. Finally, for systems with more than two electrons, the projection operators required by the method are simply and *exactly* constructed from the known zeroth-order wave functions of the target ion, rather than via the more complex procedures required by the standard Feshbach method.

In the present paper results for the resonance positions and widths of the $2s2p$ singlet and triplet autoionizing states of heliumlike atoms are presented in both a projected and nonprojected formulation. The rapid convergence of the expansion coefficients for both the energy and width of the triplet series is particularly striking. The tables present results for the isoelectronic sequence up to Ne^{8+}, but these can easily be extended to higher Z with the perturbation expansion coefficients presented here. These results are in very good agreement with accurate theoretical results obtained by variational methods as well as with experimental results, where these are available.

The results for the nonprojected calculations are of special interest as this particular method is extremely simple to implement. Indeed, this method introduces only one additional complication: the presence of avoided crossings in the optimization curve. That this might not present serious difficulties is borne out by the accuracy of the results obtained here with this method.

Work is presently underway to extend the application of the methods developed here to more highly excited autoionizing states of the two-electron ions and to the corresponding doubly excited states of the lithium isoelectronic sequence.

APPENDIX

The matrix element to be evaluated for the lowest-order contribution to the width is

$$J_s=\left\langle \psi_0^{2s2p}\left|\frac{1}{r_{12}}\right|\psi_0^{1skp}\right\rangle , \tag{A1}$$

where $\psi_0^{2s2p}=2^{-1/2}[\psi_{2s(1)2p(2)}+(-1)^s\psi_{2p(1)2s(2)}]$ and $\psi_0^{1skp}=2^{-1/2}[\psi_{1s(1)kp(2)}+(-1)^s\psi_{kp(1)1s(2)}]$ with $s=0,1$ for the singlet and triplet states, respectively. The $\psi_{nl(i)}$ represent normalized hydrogenic orbitals and

$$\psi_{kp}=A_k r(\cos\theta)\Phi\left(2+\frac{i}{k}\middle|4\middle|2ikr\right)\exp(-ikr) . \tag{A2}$$

Here, $k=2^{-1/2}$, $A_k=3^{-1/2}k\{[1+k^{-2}]/[1-\exp(-2\pi/k)]\}^{1/2}$, and Φ is a confluent hypergeometric function. Then,

$$\begin{aligned}J_s=\tfrac{8}{27}A_k(&[\tfrac{1}{2}I_5(2)+\tfrac{1}{3}I_4(2)]\delta_{s,0}\\&+(-1)^{s+1}\tfrac{4}{9}\{I_3(2)+\tfrac{8}{3}[I_2(2)+I_1(2)+\tfrac{1}{2}I_2(\tfrac{1}{2})\\&-I_1(\tfrac{1}{2})]\}) .\end{aligned} \tag{A3}$$

The auxiliary integrals

$$I_n(\alpha)=\int_0^\infty dx\, x^n\Phi\left(2+\frac{i}{k}\middle|4\middle|2ikx\right)\exp[-(\alpha+ik)x] \tag{A4}$$

can be evaluated given the recursion relation

$$\begin{aligned}I_{n+1}(\alpha)=\{&2[(n-1)\alpha-1]I_n(\alpha)-n(n-3)I_{n-1}(\alpha)\}\\&\times[\alpha^2+k^2]^{-1}\end{aligned} \tag{A5}$$

and the starting value

$$I_3(\alpha)=6(\alpha^2+k^2)^{-2}\exp\left[-\frac{2}{k}\tan^{-1}(k/\alpha)\right] . \tag{A6}$$

Substituting values of n from 0 to 4 in (A5) yields expressions for all needed I_n. In the calculation of the total width, only the additional integrals

$$\begin{aligned}K_{n,m}(\alpha,\beta)=\int_0^\infty dx\, x^n\Phi&\left(2+\frac{i}{k}\middle|4\middle|2ikx\right)\\&\times\exp[-(\alpha+ik)x]\int_x^\infty dy\, y^m\exp(-\beta y)\end{aligned} \tag{A7}$$

are required. These are easily generated from the relation

$$K_{n,m}(\alpha,\beta)=\frac{1}{\beta}[I_{n+m}(\alpha+\beta)+mK_{n,m-1}(\alpha,\beta)] . \tag{A8}$$

The $K_{n,0}$ are first obtained from the corresponding I_n, followed by an upward recursion on the second index, m.

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